



## REPORT DOCUMENTATION PAGE

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2

1 AGENCY USE ONLY (Leave Blank)

2. REPORT DATE

3. REPORT TYPE AND DATES COVERED

September 1991

Final Technical: 9/1/81 - 10/31/87

4. TITLE AND SUBTITLE

5. FUNDING NUMBERS

OPTICAL &amp; ACCOUSTICAL SPECTROSCOPY OF SOLIDS

N00014-82-K-0089

6. AUTHOR(S)

Professor Eli Burstein

7. PERFORMING ORGANIZATION NAME

University of Pennsylvania  
Philadelphia, Pennsylvania 191048. PERFORMING ORGANIZATION  
REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) ADDRESS(ES)

Office of Naval Research  
Washington, DC 2037510. SPONSORING AGENCY  
REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT

Research areas discussed are: Optical Properties of Molecules Adsorbed at Metal Surfaces; Valence Electron Excitations of Atoms Adsorbed at Metal Surfaces; Raman Scattering Excitation-Profile Spectra of Molecules Adsorbed at Metal Surfaces; Resonant Raman Scattering by Molecules Adsorbed on Smooth Noble Metal Surfaces; Luminescence of Dye Molecules Adsorbed at Ag Surfaces; Optical Phenomena at Silver Surfaces with Submicroscope Bumps; Nonlocal Dielectric Response of Rough Metal Surfaces; Second Harmonic Generation by Molecules Adsorbed at Metal Surfaces; Two-Photon Excitation of Luminescence by Noble Metals; Coherent Three-Wave Frequency Mixing at Semiconductor Surfaces; and Narrow Beam Excitation of Electromagnetic Modes in Prism Configurations

14. SUBJECT TERMS

Adsorbed, Metal, Surfaces, Valence, Electron, Excitations, Raman Scattering, Excitation, Spectra, Noble, Luminescence, Dye Molecules, Optical, Dielectric Second Harmonic, Generation, Two-Photon, Coherent, Semiconductor, Prism

15. NUMBER OF PAGES

13

16. PRICE CODE

17. SECURITY CLASSIFICATION  
OF REPORT

Unlimited

18. SECURITY CLASSIFICATION  
OF THIS PAGE

Unlimited

18. SECURITY CLASSIFICATION  
OF ABSTRACT

Unlimited

20. LIMITATION OF ABSTRACT

Unlimited

OFFICE OF NAVAL RESEARCH

FINAL TECHNICAL REPORT

for

Contract N00014-82-K-0089

November 1, 1981 to October 31, 1987

OPTICAL AND ACOUSTICAL SPECTROSCOPY OF SOLIDS

ELECTROMAGNETIC PHENOMENA AT SURFACES

Elias Burstein

University of Pennsylvania

Philadelphia, PA 19104

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## RESEARCH CARRIED OUT UNDER CONTRACT N00014-82-K-0089

### OPTICAL PROPERTIES OF MOLECULES ADSORBED AT METAL SURFACES

The experimental and theoretical investigations of the "surface enhanced" Raman scattering (SERS) by molecules adsorbed on metals have focussed on the role played by surface roughness in enhancing the incident and scattered EM field and on the radiative excitation and recombination of electron-hole pairs. We have pointed out that the Raman scattering cross-sections of adsorbed molecules also involve contributions from adsorbate-substrate "intermolecular" (e.g., bonding-antibonding and charge-transfer) electronic excitations that are absent in the "isolated" molecules. The linear and nonlinear optical properties of adsorbed molecules are thus more appropriately viewed, even in the case of physisorbed molecules, as the properties of adsorbate-substrate complexes whose electronic excitations interact with the single particle and collective electronic excitations of the underlying substrate<sup>1</sup>. The increase in the Raman scattering cross-section of the adsorbed molecules due to contributions from "intermolecular" electronic excitations is not a surface enhancement, but rather is a consequence of the formation of a new molecular species, e.g., the adsorbate-substrate complex.

### THE VALENCE ELECTRON EXCITATIONS OF ATOMS ADSORBED AT METAL SURFACES.

We have investigated theoretically the charge-transfer excitations of atomic adsorbates on metal surfaces and the vibronic aspects of the charge transfer excitations which arise from the different dependence of the ground and excited states on the adsorbate-substrate separation<sup>1</sup>. In the case of Cl adsorbed on an Al substrate, there is a charge transfer of an electron from the Al to the Cl in the ground state. The charge-transfer excitation involves the transfer of an electron from the Cl<sup>-</sup> to an empty level

in the metal substrate leaving a (neutral) Cl atom adsorbed at the surface. The electronic transitions between the ground state and the excited state correspond to vibronic transitions. The optical matrix elements involve Franck-Condon factors whose magnitudes depend on the overlap of the vibrational wavefunction of the ground ( $\text{Cl}^-$ ) state and the excited (Cl atom) state. The vibronic character of the charge-transfer excitations plays a key role in the Raman scattering by the adsorbate-substrate ( $\text{Cl}^-$ -Al) complex and is one of the factors that determine the Raman scattering cross-section by the  $\text{Cl}^-$ -Al vibration modes.

#### RAMAN SCATTERING EXCITATION-PROFILE SPECTRA OF MOLECULES ADSORBED AT METAL SURFACES

We have demonstrated that Raman scattering by adsorbed molecules on metal surfaces can be used as a surface-sensitive probe of the electronic excitation of the adsorbate-substrate complexes that are formed<sup>2-4</sup>. The measurement of the excitation-profiles of the Raman scattering by the different vibration modes of the adsorbate-substrate complex is, in fact, a form of *modulation spectroscopy* in which the vibration modes provide the "modulation field". It yields information, not only about the energies, widths and strengths of the valence electron excitation, from which one can obtain information about the excited states of the adsorbate-substrate complex, but also about the vibronic character of the electronic states involved and about the underlying Raman scattering mechanism. We have measured the Raman scattering-excitation profile spectra for totally symmetric and non-totally symmetric vibration modes of free base phthalocyanine molecules adsorbed on Ag in UHV and have obtained information about the energies, widths and vibronic character of the singlet  $\pi - \pi^*$  valence electron excitations<sup>2,3</sup>. From the polarization dependence of the resonant peak in the RS-EP spectra we find that there are no appreciable  $xz$ ,  $yz$  or  $zz$  components of the Raman scattering tensor, which suggests that the character of the singlet  $\pi - \pi^*$  vibronic excitations are not qualitatively different from that of the free

molecule and that the  $n$  electrons are not primarily involved in the bonding of the molecules to the metal substrate. The resonant Raman scattering at the  $\pi - \pi^*$  resonance is due primarily to a Herzberg-Teller mechanism. The data show that the  $Q_x$  and  $Q_y$  electronic excitations are red-shifted relative to those of the free molecules and the  $Q_x - Q_y$  energy separation is reduced by a factor of two. This is attributed to the weakening of the hydrogen bonds at the central nitrogen atoms that results from the bonding of the molecules to the substrate via the lone pair electrons of the central nitrogen atoms.

#### RESONANT RAMAN SCATTERING BY MOLECULES ADSORBED ON SMOOTH NOBLE METAL SURFACES

The enhanced Raman scattering by molecules adsorbed on rough noble metal substrates is due in part to the enhancement of the macroscopic and local EM fields by surface roughness and by image dipole, contributions, and in part to contributions from "intermolecular" (e.g., charge-transfer) electronic excitations of the adsorbed atoms and molecules that are absent in the free atoms and molecules. In order to observe Raman scattering by a monolayer (or submonolayer) of adsorbed molecules on a smooth metal surface, i.e., in the absence of surface enhancement of the incident and scattered field, Raman scattering measurements need to be carried out under resonance enhanced conditions, i.e., using excitation wavelengths at which the intramolecular or intermolecular resonances occur. We have carried out measurement of the polarization-dependent Raman scattering-excitation profile (RS-EP) spectra for the totally symmetric central-carbon breathing mode of crystal violet chloride adsorbed on a smooth Au surface in UHV using scattering configuration in which the incident and scattered planes are either parallel or perpendicular to one another<sup>4,5</sup>. The RS-EP spectra for this mode exhibits a sizeable resonance peak when the incident and scattering planes are parallel. This resonance peak, which corresponds to the singlet  $n - n^*$  electronic excitation of adsorbed carbonium ions ( $CV^+$ ) is not observed when the incident and scattered planes are

perpendicular, showing that the contributions from the  $\pi - \pi^*$  electronic excitation of the adsorbed to the Raman tensor of the adsorbed CV<sup>+</sup> involve only xx and yy components. On the other hand the RS-EP spectrum for the perpendicular planes scattering configuration with p-polarized incident and scattered radiation, which involves the zz component of the Raman tensor, exhibits a steadily rising scattering intensity with wavelength. We infer from the absence of the  $\pi - \pi^*$  resonance in the zz component EP spectrum that the adsorbed molecules lie flat on the metal surface, and we attribute the sizeable zz component of the Raman tensor to an "intermolecular charge-transfer electronic excitation of the adsorbate-substrate complex. These results clearly demonstrate the effectiveness of polarization-resolved RS-EP spectra for obtaining information about the energies, widths and vibronic character of the valence electron excitations of molecules adsorbed on smooth metal surfaces and, particularly about the RS mechanisms.

#### LUMINESCENCE OF DYE MOLECULES ADSORBED AT A Ag SURFACE

The quenching of the luminescence of molecules adsorbed at a smooth Ag surface is offset by the enhancement of the incident and emitted EM field when they are adsorbed at a Ag island film<sup>6,7</sup>. The observed spectra exhibit hot and relaxed luminescence components. The observed enhancement of the RS and luminescence of molecules is attributed to the "amplification" of the em field which results from the resonant excitation of collective electron oscillations in the metal islands. The magnitudes of the enhancements depend on the dielectric and structural properties of the islands, as well as on the extent to which the excitation and emission frequencies overlap the collective electron resonance bands. Under optimum conditions, the RS by molecules adsorbed on a Ag island film can be  $10^5$  times more intense than that of the isolated molecule. In the case of the luminescence, the corresponding intensity ratio (e.g., for molecules adsorbed at a Ag island film relative to that for molecules adsorbed on glass) is much smaller. The nonradiative de-excitation of the luminescent

states of the molecules by the metal offsets the effects of the field amplifications, thereby limiting the apparent enhancement of the luminescence.

#### OPTICAL PHENOMENA AT SILVER SURFACES WITH SUBMICROSCOPIC BUMPS

We have investigated the reflectance and inelastic-light scattering spectra of a silver surface with highly uniform submicroscopic bumps that was fabricated by depositing a silver film onto a silica plate that had been irradiated by normally incident 63-MeV  $^{63}\text{Cu}^{8+}$  particles and then etched to produce conical shaped etch pits<sup>8</sup>. The reflectance spectra exhibit two absorption bands, corresponding to localized plasmons of the silver bumps which oscillate in directions parallel and perpendicular to the surface. Addition of rhodamine-6 dye molecules to the surface yields marked changes in the reflection spectra. The intensities of the luminescence and the Raman scattering from the dye layer at the surface increase in approximate proportion to the number density of bumps, confirming the role of the bumps as signal amplifiers in the enhancement of the inelastically scattered light. Our data unambiguously demonstrate the enhancements of optical absorption, Raman scattering and luminescence that are due to the localized plasmons of the bumps on the Ag surface.

#### THE NONLOCAL DIELECTRIC RESPONSE OF ROUGH METAL SURFACES

The non-local dielectric response of a metal (i.e., the dependence on wavevector as well as on the frequency of the EM field) is due largely to the excitation of electron-hole pairs by the electric field component normal to the surface<sup>9</sup>. A characteristic feature is the large difference in the response of a smooth metal surface to s-polarized and p-polarized EM radiation. The random roughness of a flat continuous metal film can be characterized geometrically by a random distribution of grating, which serve to couple the incident EM radiation to surface-EM modes, and when the

superposition includes grating with large wavevectors, the grating also serve to couple the EM radiation with electron-hole pair excitations in the metal. Moreover, the marked distinction between s-polarized and p-polarized radiation tends to disappear. The rough metal surface also contains geometrical structures (e.g., bumps, pits) that act to "confine" the motion of the electrons associated with them. The collective oscillations of the electrons in these structures exhibit resonances that correspond to "localized" plasmons. The resonant frequencies for the oscillations parallel and perpendicular to the plane of the surface are in general different. It is the excitations of the localized plasmons that is responsible for the enhancement of the incident and scattered EM field in surface enhanced Raman scattering. We have investigated the EM properties of small metal particles whose dimension are smaller than the wavelength (or penetration depth of the EM radiation interacting with them)<sup>10,11</sup>. The EM field within the metal particle exhibit characteristic spatial oscillations, similar to those for a smooth metal surface, that arise from the excitation and recombination of electron-hole pairs. We find that the nonlocal response of small metal particles leads to a red shift of the localized plasmon frequency. Moreover, the contribution from electron-hole pair excitations dominates the optical absorption of the particles, in contrast to the case of the smooth planar surface where they make up a small part (e.g., about 5%) of the total absorption.

#### SECOND HARMONIC GENERATION BY MOLECULES ADSORBED AT METAL SURFACES.

Measurements of the surface roughness enhance second harmonic generation by molecules adsorbed on a Ag electrode have shown that the SHG signal for adsorbed pyrazine molecules which possess a center of inversion is comparable in magnitude to that for adsorbed pyridine molecules which lack a center of inversion. The fact that an atomic adsorbate (eg,  $\text{Cl}^-$ ) also exhibits a sizeable SHG led us to conclude that the observed SHG by the adsorbed atoms and molecules may be due



to intermolecular electronic excitations and specifically to charge-transfer excitations of the adsorbate-substrate complexes that are formed. Specifically we proposed a two level, three step charge-transfer excitation mechanism for the SHG by adsorbates at a metal surface<sup>12</sup>. It involves a charge-transfer transition induced by p-polarized photons in the first and third step, in which an electron is transferred between the metal and the affinity level of the adsorbed molecule (in the case of molecules such as pyrazine and pyridine that are adsorbed as neutral species) and a p-polarized photon driven dipole of the excited (intermediate) state in the second step. Because of the large charge-separation in the intermediate state, the optical matrix element for the second step is large. As a consequence each of the three steps involve sizeable optical matrix elements.

#### TWO-PHOTON EXCITATION OF LUMINESCENCE BY NOBLE METALS

The secondary light emission spectrum due to two-photon excitation of electron-hole pairs, which is only observed for a rough Ag surface, exhibits a broad structure with a high energy cut-off at the threshold for s-p interband transitions at the L point which is independent of the exciting photon energy<sup>13</sup>. The observed two-photon excited secondary light emission by Ag is attributed to electron-hole pair recombination transitions at the L point. The fact that the emission is only observed for a rough Ag surface indicates that the two-photon excitation of electron-hole pairs occurs at the surface and that one (or both) of the two photon excitation steps therefore involves an intraband electron-hole pair excitation. We propose that the two-photon secondary light emission excitation process involves a surface roughness-induced intraband electron-hole pair excitation step, followed by an interband electron-hole pair excitation step, which is then followed by an interband electron-hole pair recombination step.

#### COHERENT THREE-WAVE FREQUENCY MIXING AT SEMICONDUCTOR SURFACES

We have explored the basic concepts and microscopic mechanisms that play a role in coherent three-wave frequency mixing (second harmonic

generation, sum frequency generation and difference frequency generation) at semiconductor surfaces at which there are sizeable space-charge fields<sup>14</sup>. Moreover, we have suggested that 3WFM can be used as a modulation spectroscopic probe of the electronic excitations, and in particular, that resonant 3WFM can be used to probe the quantized energy levels of the carriers in depletion and accumulation layers in heterojunctions and in quantum wells<sup>15</sup>.

#### NARROW BEAM EXCITATION OF ELECTROMAGNETIC MODES IN PRISM CONFIGURATIONS

The modes that exist in an Otto ATR configuration are leaky surface EM waves and TM and TE Fabry-Perot modes. When excited by volume EM radiation of finite beam width, the leaky modes build up along the excitation region and propagate as free damped waves beyond<sup>16</sup>. Correspondingly, the spatial dependence of the reflected volume EM intensity exhibits a double-peaked interference structure at the leading edge of the excitation region followed by an exponential decay beyond. The appearance of a second peak is due primarily to a destructive interference between a mirror reflected field and a radiated field which are  $180^\circ$  out of phase. The phase velocity and the propagation length of the leaking modes can be determined from the coupling angle and the exponential decay, respectively. When the incident angle is scanned the angular dependence of the reflected intensity exhibits ATR-type minima from the excitation region and peaks from the free-wave region. A study of these peaks provides a tool for the spectroscopic study of overlayers.

PUBLICATIONS DESCRIBING RESEARCH SUPPORTED BY ONR  
UNDER CONTRACT N00014-82-K-0089

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## HONORS

E. Burstein was awarded the honorary degree of Doctor of Science by Brooklyn College of the City University of New York, June, 1985.

E. Burstein was awarded the 1986 Frank Isakson Prize of the American Physical Society for Optical Effects in Solids.